



Poly(arylene ether sulfone)s ionomers containing quaternized triptycene groups for alkaline fuel cell

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HIGHLIGHTS

- Poly(arylene ether sulfone) with quaternized triptycene groups were synthesized.
- The membranes based on these ionomers have low water uptake and high ion conductivity.
- The membranes were stable in alkaline conditions.

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ABSTRACT

A series of poly(arylene ether sulfone)s containing quaternized triptycene groups are synthesized through a chloromethylation reaction following a quaternization process. The resulting ionomers are soluble in polar aprotic solvents; thus, flexible, tough membranes could be prepared by solution casting. Novel anion exchange membranes based on these ionomers are obtained by anion exchange with hydroxide ions. All anion exchange membranes show conductivities above $10^{-2} \text{ S cm}^{-1}$ at room temperature. The highest hydroxide conductivity is $7.2 \times 10^{-2} \text{ S cm}^{-1}$, which is achieved by the anion exchange membrane with ion exchange capacity (IEC) = 2.61 mmol g^{-1} . Meanwhile, these anion exchange membranes have low water uptake and good dimensional stability even at high IEC values. For example, the membrane water uptake (IEC = 1.97 mmol g^{-1}) is only 21% at room temperature, and the swelling ratio is 11%. The anion exchange membranes are stable in alkaline conditions. All the membranes have no significant change in 4 M NaOH solution at 25 °C after 30 days. All results suggest that these anion exchange membranes have potential application in alkaline fuel cells.

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1. Introduction

Fuel cells are considered as a promising future energy conversion technology because of their high energy density, high efficiency and quiet environmental friendly operation, as well as low maintenance costs [1]. Proton exchange membrane fuel cells (PEMFCs), which use proton exchange membranes as the electrolyte and function in acidic medium, are well known. However, there are still some obstacles prevent PEMFCs from widespread commercialization, including slow electrode kinetics, the high cost and low durability of the catalyst, and high fuel crossover [2]. Recently, interest has grown in the development of anion exchange membrane fuel cells (AEMFCs), since they have the potential to overcome these hurdles of PEMFCs by switching from an acidic

medium to a basic medium. In basic medium, the cathode oxygen reduction over-potential could be reduced dramatically relative to that in acidic medium. The reduced over-potential resulted in high fuel cell efficiencies, and the kinetics of oxygen reduction reactions were faster. As a result, non-noble metals, such as nickel and silver, could be used as catalysts [3]. Moreover, the metal catalysts were more durable in basic medium. Furthermore, the choices of fuels were more flexible, many kinds of fuels (e.g., methanol, ethanol, and ethylene glycol) could be used, because of the low over-potential for hydrocarbon fuel oxidation and reduced fuel crossover [4–6].

Anion exchange membranes (AEMs), key components of AEMFCs, serve to transport anions from cathode to anode, separate fuel and oxidant, and support the catalyst. However, the commercially available AEMs based on cross-linked polystyrene, are not suitable for fuel cell application, because of their low hydroxide conductivity and poor stability in alkaline or electrochemical environments. Nowadays, most of the researches about AEMs for

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alkaline fuel cells were related to developing quaternized polymers that employed quaternary ammonium groups as ion conducting groups. Many kinds of polymers have been quaternized and used as anion exchange membrane materials, such as poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(vinylidene fluoride) (PVDF) [7–9], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [10–13], poly(phenylene) [14] poly(vinyl alcohol) [15,16], and poly(arylene ether sulfone) [17–20]. Quaternized block polymers based AEMS were also reported by several groups [21,22]. These block polymers based AEMS exhibited higher conductivities than random polymer based AEMS, because of their unique hydrophobic/hydrophilic phase separation and well-interconnected ion transporting pathways. Recently, ionomers with a guanidinium group, quaternary phosphonium group and imidazolium group were used to prepare AEMS [23–25].

The primary problem with using AEMS is the membrane conductivity and the membrane stability. AEMS with high water uptake values exhibited high conductivities, but membranes' swelling ratios were also high, which reduce their mechanical strength. The AEMS, which could be used in cell assemble, should have enough mechanical strength. Earlier research showed that introducing rigidity, bulkiness, and high hydrophobicity fluorenyl [26] or binaphthyl groups [27] into the polymer backbone resulted in PEMs with low water uptake and swelling ratios, but high ion exchange capacities and conductivities. In our previous studies, triptycene groups were sulfonated to prepare PEMs [28]. We found that the obtained proton exchange membranes showed high thermal stability and mechanical strength at low humidity regardless of high ion exchange capacity. Meanwhile, the membranes achieve high proton conductivity in a wide range of humidity at 80 °C. Herein, we report a series of quaternized poly(arylene ether sulfone) based AEMS, which contain quaternized triptycene groups. As we expected, the AEMS had high hydroxide conductivity, as well as low water uptake and dimensional stability even at high IEC value.

2. Experimental

2.1. Materials

4,4'-Difluorodiphenylsulfone (DFDPS), bis(4-hydroxyphenol) sulfone (BPS) and chloromethyl methyl ether (CMME) were purchased from Aldrich. Anthracene, quinone, hydrobromic acid (40%) and zinc chloride were purchased from China National Pharmaceutical Group Corporation. Zinc chloride was dried at 100 °C for 24 h before used. *N*-methyl-2-pyrrolidone (NMP) was stirred over CaH₂ for 24 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves under a nitrogen atmosphere. All other reagents were obtained from commercial sources and used as received. The poly(arylene ether sulfone)s containing triptycene groups (PES-*x*) were prepared as previous described [28].

2.2. Synthesis of poly(arylene ether sulfone)s containing chloromethyl groups (PESCM-*x*)

The PESCM-*x*, where *x* refers to the percentage of triptycene repeat unit in unfunctionalized polymers, was synthesized through a modified chloromethylation process. A typical synthetic procedure of PESCM-50 was as follows. To a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser were added PES-50 (1.0 g, 2.0 mmol) and tetrachloroethane (30 mL). The mixture was stirred adequately to form homogeneous solution. Anhydrous

zinc chloride (0.39 g, 6.0 mmol) was dissolved in chloromethyl methyl ether (7.5 mL). Then the zinc chloride solution in CMME was added into the flask under nitrogen. The resulting solution was heated to 60 °C for 18 h. After that, the mixture was cooled to room temperature and coagulated in ethanol with vigorous stirring. The resulting fiber-like polymer was washed with ethanol several times and dried under vacuum for 24 h at 60 °C before used.

2.3. Preparation of quaternized poly(arylene ether sulfone)s (QPES-*x*)

The PESCM-*x* was quaternized by dry trimethylamine gas in DMSO at 40 °C. A typical process was as follows: PESCM-*x* (2 g) was dissolved in DMSO (40 mL) to form a solution of 5 wt %. The solution was heated to 40 °C. Meanwhile, dry trimethylamine gas was introduced to the solution. The mixture was kept on bubbling with dry trimethylamine gas at 40 °C for 4 h. After that, the solution was kept at 40 °C for another 4 h. Then the solution was cooled to room temperature, and poured into excessive acetone. The fiber-like precipitate was collected and washed with acetone several times. Then it was dried under vacuum at 80 °C for 24 h before used.

2.4. Preparation of anion exchange membranes

QPES-*x* membranes were prepared as follows: QPES-*x* ionomer (0.8 g) was dissolved in DMSO (10 mL). The solution was filtrated to removed impurity and bubbles. Then the solution was cast onto a clean flat glass dish. The membrane was dried at 80 °C for 12 h, and at 120 °C under vacuum for 24 h. After that the QPES-*x* membrane was peeled off and immersed in 1 mol L⁻¹ NaOH aqueous solution for 48 h to make the membrane change into OH⁻¹ form. Finally, the membrane was washed adequately and kept in deionized water for 48 h to remove residual NaOH. The QPES-*x* membrane was kept in deionized water before used.

2.5. Membrane characterization

2.5.1. Measurements

¹H NMR spectra were measured at 300 MHz on an AV300 spectrometer. Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin–Elmer TGA-2 thermogravimetric analyzer from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ in N₂. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 10 mm min⁻¹, and the testing membranes were cut into 40 × 5 mm rectangle samples. FT-IR spectra were recoded on membranes samples using a Bio-Raddigilab Division FTS-80 FT-IR spectrometer.

2.5.2. Ion exchange capacity (IEC)

The IECs of the copolymer membranes in OH⁻¹ form were measured by titration. The OH⁻¹ form membranes were immersed in HCl (0.02 M) standard solution at room temperature (25 °C) for 48 h. Then the HCl solution was titrated with a standardized NaOH aqueous solution using phenolphthalein as an indicator.

2.5.3. Water uptake and dimensional change

The water uptake and swelling ratio of the anion exchange membranes were measured as follows: The membranes were dried under vacuum at 100 °C until their weight did not change any more to obtain dry materials. They were immersed in deionized water for 4 h at a given temperature. Then the

membranes were wiped with tissue paper, and measured their weight quickly. The water uptake (WU) of QPES- x membranes were calculated according to:

$$WU(\%) = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \quad (1)$$

Here W_{dry} and W_{wet} are the weight of the dry and the corresponding water-swollen membranes, respectively.

The dry membranes were chopped into circular samples, and measured their diameter in dry condition. Then the samples were immersed in deionized water for 4 h at given temperature. They were taken out and measured their diameter in wet condition. The swelling ratio (SR) of the membranes was calculated from:

$$SR(\%) = \frac{(l_{\text{wet}} - l_{\text{dry}})}{l_{\text{dry}}} \times 100 \quad (2)$$

Here, l_{dry} and l_{wet} are the diameter of the dry and wet samples, respectively.

2.5.4. Hydroxide conductivity

The hydroxide conductivities (σ , S cm^{-1}) of the copolymer membranes (size: 1 cm \times 4 cm) were obtained using $\sigma = d/LsWsR$ (d : distance between reference electrodes, and Ls and Ws are the thickness and width of the membrane respectively). Here, ohmic resistance (R) was measured by four-point probe

alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h prior to measurement. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10-min interval until no more change in conductivity was observed.

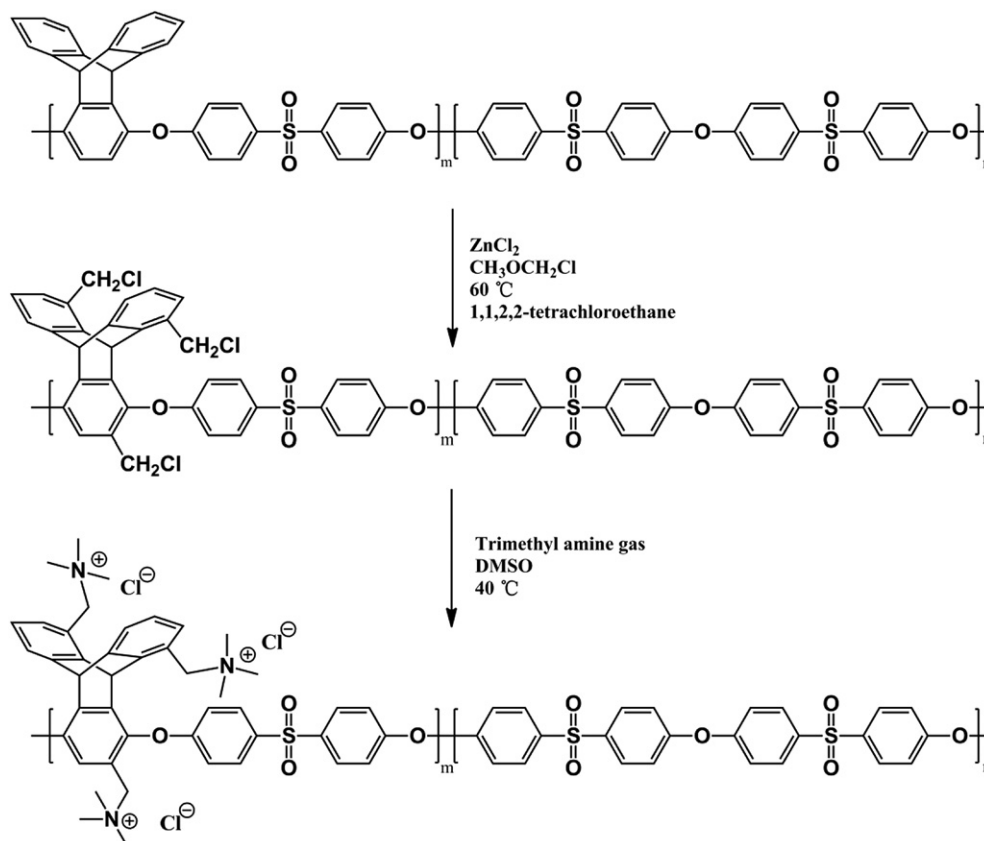
2.5.5. The alkaline stability of the AEMs

The QPES- x membrane samples were kept in a NaOH solution (4.0 M) at 25 °C for a certain time. Then we observed the shape of the test sample after being shaken lightly. Furthermore, the alkaline stability was determined from changes in the IEC and conductivity of the test samples.

3. Results and discussion

3.1. Synthesis and characterization of the QPES- x

As shown in Scheme 1, the PESCM- x copolymers were prepared via a modified chloromethylation reaction, which was performed



Scheme 1. Synthesis of PESCM- x copolymers.

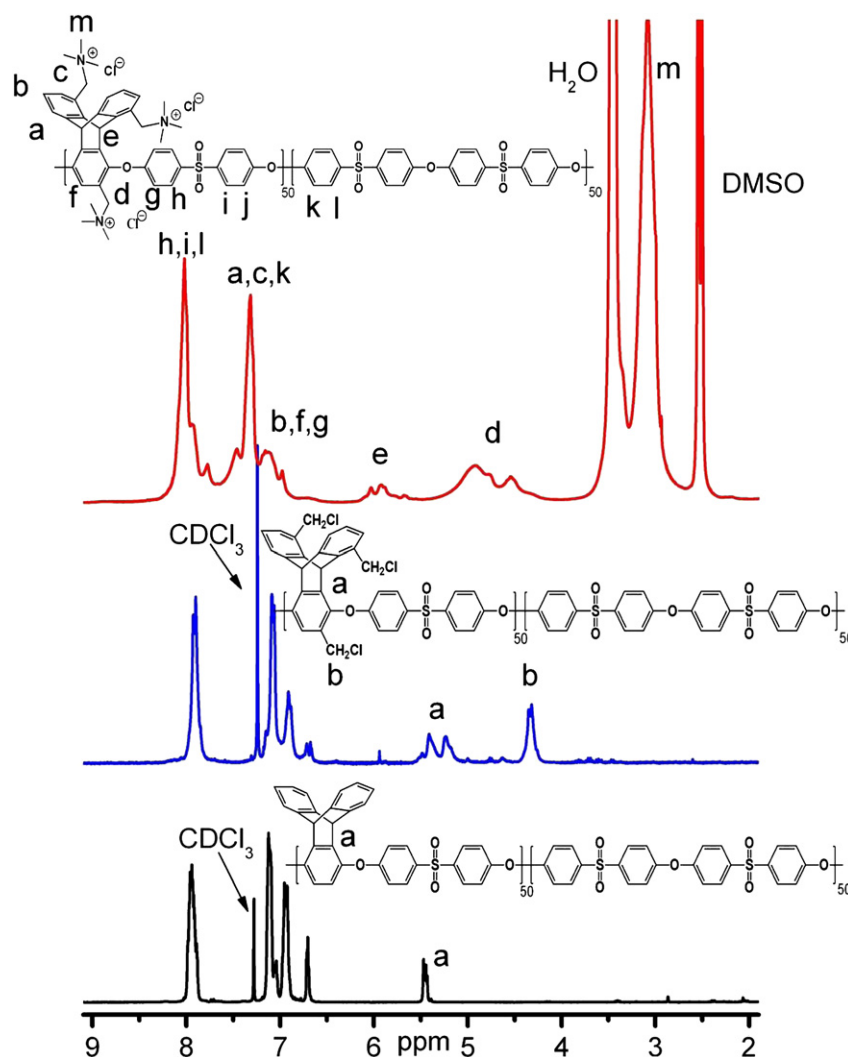


Fig. 1. ^1H spectra of PES-50, PESCM-50 in CDCl_3 and QPES-50 in $\text{DMSO}-d_6$.

in 1,1,2,2-tetrachloroethane using chloromethyl methyl ether (CMME) as a chloromethylation reagent and ZnCl_2 as the catalyst. The ^1H NMR spectroscopy of PES-50, totally chloromethylated PESCM-50 and QPES-50 are shown in Fig. 1. For the PESCM-50, the peaks at about δ 4.5 were the chemical shifts of Hb on the chloromethyl group. The peaks at about δ 5.5 were assigned to the Ha on triptycene groups. They split into multiple peaks because of the isomerism of triptycene groups as previous reported [28]. The DF (degree of function) values were calculated from the ratio of the integration of Hb and Ha. We investigated the effect of reaction conditions such as the reaction temperature, reaction time, and the amount of CMME and ZnCl_2 , using PES-50 as an example, and the results are shown in Fig. 2. The optimized reaction conditions were as follows: CMME, 60 equivalents (to the triptycene repeat units); ZnCl_2 , 3.0 equivalents; reaction temperature, 60°C ; and reaction time, 18 h. In our previous research of poly(arylene ether sulfone) chloromethylation reaction [23], the reaction conditions must be controlled carefully to avoid gelation. In this work, we found no gelation happen during the chloromethylation reaction of PES-*x*, for we chose BPS as the copolymerization monomer. In the BPS repeat units each aromatic ring was connected with an electron-withdrawing sulfone group, and cross-linking via Friedel–Crafts alkylation by the chloromethyl groups could not occur. As compared with the conditions used in our previous paper [23], we used a higher reaction temperature, more CMME,

and a longer reaction time to prepared totally chloromethylated PESCM-*x*.

The PESCM-*x* copolymers were quaternized by reaction with dry trimethylamine gas to prepare QPES-*x* ionomers. The PESCM-*x* copolymer was dissolved in DMSO, and the solution was bubbled

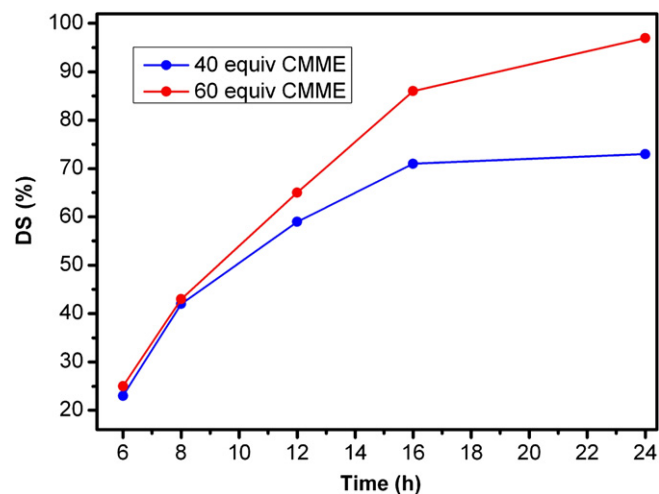


Fig. 2. Effect of the amount of CMME and reaction time on the DF of PES-50.

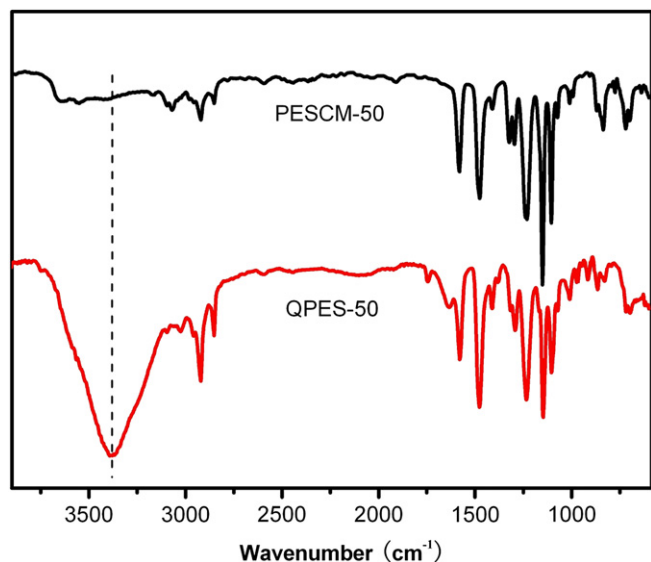


Fig. 3. The IR spectra of PES-50 and QPES-50.

with dried trimethylamine gas for 4 h at 40 °C. The solution was kept at 40 °C for another 4 h to ensure that all the chloromethyl groups were converted into quaternary ammonium groups. The viscosity of the solutions became higher during the quaternization process, because of the polymer chain extension, which was caused by the repulsion of quaternary ammonium groups located along the polymer backbone. In the ^1H NMR spectroscopy of QPES-50 (Fig. 1), the peaks at about δ 3.2 were assigned to the protons on the methyl group of quaternary ammonium groups. This confirms that the chloromethyl groups were quaternized successfully.

The FT-IR spectra of PESCM-50 and QPES-50 are shown in Fig. 3 to further confirm the structure of these copolymers. The absorption bands at $2925\text{--}2848\text{ cm}^{-1}$ are characteristic of $-\text{CH}_2-$ and $-\text{CH}_3$ groups. The broad band at 3384 cm^{-1} was assigned to the stretching vibration of O–H bonds. The bands at $681\text{--}663\text{ cm}^{-1}$ arise from stretching vibrations of C–Cl bonds. These bands disappeared after quaternization, and new absorption bands at $2925\text{--}2848\text{ cm}^{-1}$ were found. The results confirm that the chloromethyl groups were converted completely into quaternary ammonium groups.

3.2. The solubility of the QPES-x ionomers and the membrane preparation

Table 1 presents the solubility of QPES-x ionomers. All the ionomers showed good solubility in polar aprotic solvents such as

Table 1
The solubility of QPES-x ionomers.

Sample	Solubility ^a					
	CHCl_3	NPA	DMF	DMAc	DMSO	NMP
QPES-25	–	–	++	++	++	++
QPES-30	–	–	++	++	++	++
QPES-35	–	–	++	++	++	++
QPES-40	–	–	++	++	++	++
QPES-45	–	–	++	++	++	++
QPES-50	–	–	++	++	++	++
QPES-55	–	+	++	++	++	++
QPES-60	–	++	++	++	++	++

^a ++: Soluble at room temperature, +: Soluble after heating, –: Insoluble.

NMP, DMF, DMAc, and DMSO at room temperature. In addition, QPES-60 also dissolved in 2-propanol. Solubility in low boiling point solvents was a necessary property for AEMs, because the soluble ionomer can be used in the catalyst layer to build an efficient three-phase boundary and reduce the internal resistance [20]. The QPES-x membranes were prepared by the way of a solution casting process. Flexible, tough membranes were prepared using the optimized drying procedure. The QPES-x membranes obtained were in chloride form, and were converted into hydroxide form by immersion in a 1 M NaOH aqueous solution at room temperature for two days.

3.3. Thermal stability of the AEMs

Thermal stability is an important factor for the AEMs, because work at elevated temperatures could enhance the reaction kinetics and reduce the thermodynamic voltage losses of AEMFCs [25]. We used thermogravimetric analysis to test QPES-x membranes' thermal stability. Fig. 4 shows the TGA curves of the QPES-x membranes. There was a slight weight loss between 60 and 180 °C. It corresponded to the evaporation of absorbed water, for the QPES-x were hydrophilic and absorbed water from the atmosphere. The similar behavior has been founded commonly in other polymeric ion exchange membranes [21]. There are two thermal degradation steps on each TGA curve except the weight loss of absorbed water. The first one around 200 °C was assigned to the degradation of quaternary ammonium groups of the QPES-x copolymers. The second one around 350 °C was attributed to the degradation of the polymer backbones.

3.4. IEC, water uptake, swelling ratio and the mechanical property of the AEMs

The water uptake of AEMs had a significant effect on their conductivity and mechanical strength. The hydroxide transport was accelerated by the water molecules in the AEMs, so AEMs with high water uptake often have high conductivity. However, the AEMs swell excessively and lose their mechanical strength if they absorb too much water. In an alkaline fuel cell, the AEMs act as fuel separator and catalyst supporter, and they need to maintain sufficient dimensional stability and mechanical strength. Therefore, it is necessary to balance water uptake and conductivity to obtain AEMs that can be used in alkaline fuel cells. Table 2

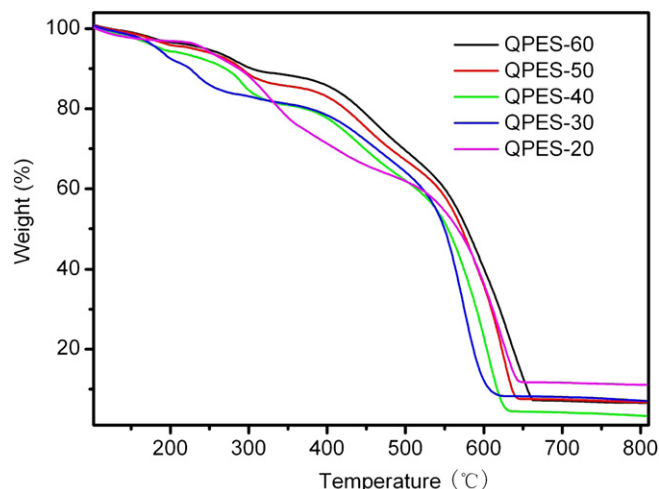


Fig. 4. The TGA curves of QPES-x membranes.

Table 2IEC, water uptake, swelling ratio and hydroxide conductivity of the QPES-*x* membranes.

Sample	IEC (m equiv g ⁻¹)		Water uptake (%)		Swelling ratio (%) ^c		Conductivity (S cm ⁻¹) ^d
	Theoretical ^a	Experimental ^b	25 °C	60 °C	25 °C	60 °C	
QPES-25	1.38	1.34	8	11	5	7	0.012
QPES-30	1.61	1.55	12	16	7	9	0.017
QPES-35	1.83	1.76	16	20	9	12	0.023
QPES-40	2.07	1.97	21	31	11	15	0.029
QPES-45	2.23	2.14	26	41	16	20	0.038
QPES-50	2.43	2.30	39	56	22	32	0.047
QPES-55	2.60	2.49	62	86	38	52	0.058
QPES-60	2.78	2.61	94	134	64	82	0.072

^a Calculated from ¹H NMR spectra.^b Determined by titration.^c The swelling ratio was in the lengthwise direction.^d The conductivity was measured at room temperature.

shows the IEC, water uptake and the swelling ratio of the QPES-*x* membranes. The water uptake value was calculated from the ratio of the weight of membranes that had absorbed water and the weight of dry membranes. As shown in Table 2, the QPES-*x* membranes water uptake and swelling ratio both increased with the IEC and temperature. In general, the water uptake of QPES-*x* membranes was lower than traditional poly(arylene ether sulfone) based AEMs. Using the QPES-30 membrane (IEC = 1.55 mmol g⁻¹) as an example, the water uptake value was 12% at 25 °C. As for the traditional poly(arylene ether sulfone) based AEM with similar IEC (IEC = 1.5 mmol g⁻¹), the water uptake value was 40% at 25 °C [20]. From the comparison, we could find that the water uptake of QPES-*x* membranes was markedly lower than that of traditional quaternized poly(arylene ether sulfone) based membranes with similar IEC. Moreover, as shown in Table 2, the QPES-*x* membrane swelling ratio was lower since it absorbed less water. For example, the swelling ratio of QPES-30 was 7% at 25 °C and 9% at 60 °C. The low swelling ratio indicated that the QPES-*x* membranes had good mechanical properties. This might be caused by the introduction of triptycene groups into the polymer main chain. The π - π interaction between polymer chains could be increased by the introduction of large conjugated triptycene groups, and the increased interaction could confine the water uptake and swelling ratio. The polymer chains with triptycene groups formed an interlocking structure to minimize free volume and fill the concave clefts of the triptycene groups. This kind of polymer chains structure may also prevent QPES-*x* membranes from swell too much. Moreover, the charged groups of QPES-*x* membranes located on the side chain, and could show lower water uptake and swelling ratio than the main-chain type.

To further confirm the benefits that get from low water uptake, we test the mechanical strength of the QPES-*x* membranes in 100% humidity, and the result was shown in Table 3. The QPES-*x* had

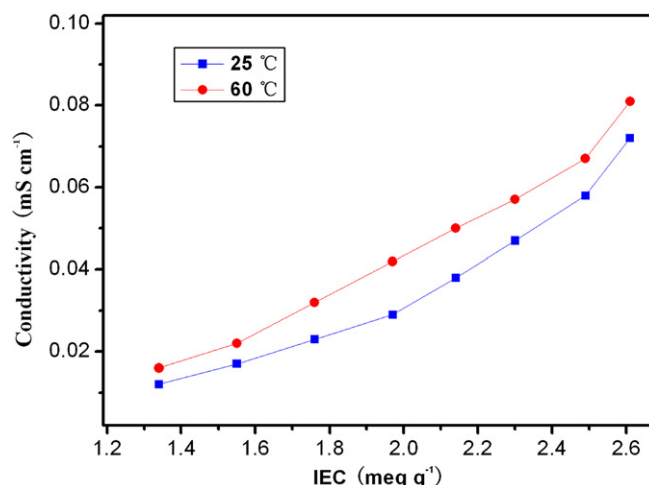
a tensile stress at maximum load of 20.3–57.2 MPa, a Young's moduli of 0.32–1.57 GPa, and an elongation at break of 11.7–42.4%. These results indicated that the QPES-*x* membranes were tough, ductile, and suitable for alkaline fuel cell applications.

3.5. Hydroxide conductivity of the AEMs

The hydroxide conductivity at different temperatures is a particularly important property of ion exchange membranes for fuel cell applications. The hydroxide conductivity of the QPES-*x* membranes was measured at different temperatures, and the results are shown in Fig. 5 as a function of the IEC. In general, the hydroxide conductivity of the QPES-*x* membranes increased with increasing IEC and temperature. The AEMs should have conductivities above 10⁻² S cm⁻¹ for alkaline fuel cell applications at room temperature. As shown in Fig. 6, all the QPES-*x* membranes showed conductivities above 10⁻² S cm⁻¹ at room temperature. The QPES-60 membrane with IEC = 2.61 mmol g⁻¹ showed the highest conductivity of 0.072 S cm⁻¹ at room temperature. In addition, the QPES-*x* membranes showed higher conductivities than traditional poly(arylene ether sulfone) based AEMs with similar IEC. For example, the conductivity of the QPES-30 membrane (IEC = 1.55 mmol g⁻¹) was 0.017 S cm⁻¹, and the conductivity of traditional poly(arylene ether sulfone) based AEMs with similar IEC was 0.01 S cm⁻¹ (IEC = 1.5 mmol g⁻¹) [20]. The high conductivity of QPES-*x* membranes is probably due to the high IEC and the dense

Table 3Mechanical properties of the QPES-*x* membranes.^a

sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
QPES-25	57.2	1.57	11.7
QPES-30	49.9	1.37	13.2
QPES-35	47.7	1.23	15.7
QPES-40	43.6	1.12	18.7
QPES-45	38.8	0.86	20.2
QPES-50	31.5	0.44	29.2
QPES-55	25.6	0.37	39.1
QPES-60	20.3	0.32	42.4

^a Measured at 25 °C, 100% RH.**Fig. 5.** The hydroxide conductivity of QPES-*x* membranes at different temperature.

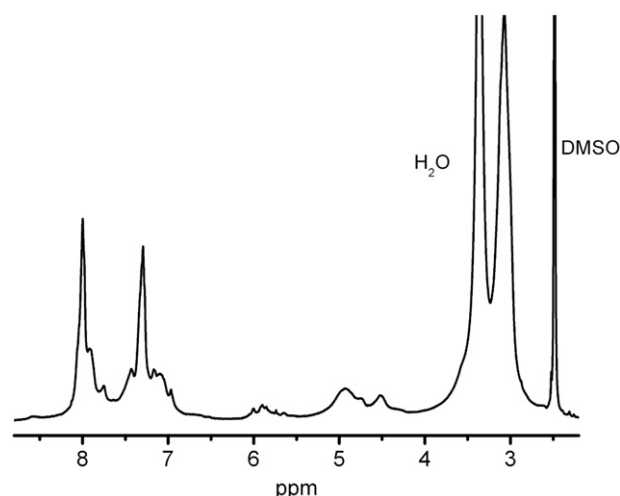


Fig. 6. ^1H spectra of QPES-50 in $\text{DMSO}-d_6$ after alkaline stability test.

distribution of the quaternary ammonium groups. The introduction of triptycene groups into the polymer backbone made QPES- x membranes durable in water even at high IEC ($>2.5 \text{ mmol g}^{-1}$), AEMs with high IEC showed high conductivity. In addition, there were three quaternary ammonium groups on each triptycene group, the dense distribution of functional groups could form good ion conductive pathway and facilitate the conductivity of hydroxide ions, so the conductivity of QPES- x membranes was higher than traditional poly(arylene ether sulfone) based AEMs with similar IEC.

3.6. The alkaline stability of AEMs

The stability of the AEMs in alkaline conditions is another important property that relates to the operation time of the AEMFCs. The alkaline stability of QPES- x membranes was determined by immersing the membranes in 4 M NaOH solution at room temperature, and the results are shown in Table 4. In basic conditions, there were two kinds degradation of the AEMs, the degradation of charge groups and the polymer backbone. The degradation of charge groups would reduce the AEMs' conductivity, and the degradation of polymer backbone would cause fragment of the AEMs. As shown in Table 4, there was no visible change in the QPES- x membranes IEC values, hydroxide conductivity or appearance after the alkaline stability test. And the ^1H spectra of QPES-50

in $\text{DMSO}-d_6$ after alkaline stability test is shown in Fig. 6, it further confirmed that the structure of QPES-50 ionomer have on significant change during the alkaline stability test. This indicated that, the QPES- x membranes were stable in alkaline condition, and they could be used in alkaline fuel cell applications.

4. Conclusions

In conclusion, a series of poly(arylene ether sulfone) with quaternary triptycene groups were prepared via a chloromethylation reaction following a quaternization process. These ionomers were soluble in polar aprotic organic solvents, and formed flexible and tough membranes via solution casting. The QPES- x membranes showed low water uptake and good dimension stability since the charged groups were attached to rigidity, bulkiness, and hydrophobic triptycene groups. In addition, the QPES- x membranes were mechanically strong even at high IEC values. Meanwhile, the conductivity of QPES- x membranes had high hydroxide conductivity. The highest conductivity was 0.072 S cm^{-1} at room temperature. This was due to the high IEC and dense distribution of the quaternary ammonium groups. Finally, the QPES- x membranes were stable in 4 M NaOH aqueous solutions for 30 days at room temperature.

Acknowledgments

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Table 4
The alkaline stability of QPES- x membrane.^a

Sample	τ^b (day)	Ratio (IEC/IEC ₀) ^c	Conductivity	
			Before	After ^d
QPES-25	>30	0.99	0.012	0.012
QPES-30	>30	1.00	0.017	0.016
QPES-35	>30	1.00	0.023	0.023
QPES-40	>30	0.98	0.029	0.029
QPES-45	>30	0.98	0.038	0.038
QPES-50	>30	0.97	0.047	0.046
QPES-55	>30	0.96	0.058	0.056
QPES-60	>30	0.97	0.072	0.070

^a 4 M NaOH solution, 25 °C.

^b The time at which the membrane showed no visible change in shape after being shaken lightly.

^c IEC₀ and IEC are the ion exchange capacity of the test before and the test after, respectively.

^d The hydroxide conductivity after the alkaline stability test (4 M NaOH, 25 °C, 48 h).